

LBL-27720 rev, Invited Paper for IEEE Circuits and Devices Magazine

## LARGE-AREA CHROMOGENICS FOR SMART WINDOWS\*

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August 1991

\*This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Technologies, Building Systems and Materials Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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**ABSTRACT**

The concept of large-area chromogenic optical switching devices for glazings is introduced. Devices can be used for dynamic control of light through building, and vehicle glazings and certain information display applications. Also, chromogenic glazings can be used for the modulation of reflector surfaces for automotive mirrors. Both visible and solar control can be obtained from these devices. Switching ranges can be from as high as 80% to 5-10% transmittance in the visible region. A selection of optical switching technologies and their properties will be compared with emphasis on electrochromic and dispersed liquid crystal devices. The science of selected electrochromic devices is covered. The optical and electrochemical properties of tungsten oxide and nickel oxide devices are detailed. The general process of electrochromism is based on the reversible dual injection of ions and electrons which induce large optical changes due to both color center formation and electronic changes in the material. Long-term memory can be maintained for several hours without a holding potential. Technical issues concerning large-scale chromogenic devices are discussed.

**KEYWORDS**

Windows, Glazings, Smart Windows, Optical Switching, Chromogenic, Electrochromism, Photochromism, Thermochromism, Liquid Crystals, Suspended Particle Device, Tungsten Oxide, Nickel Oxide, Buildings and Automobiles.

## LARGE-AREA CHROMOGENICS FOR SMART WINDOWS

Carl M. Lampert

## INTRODUCTION TO CHROMOGENICS

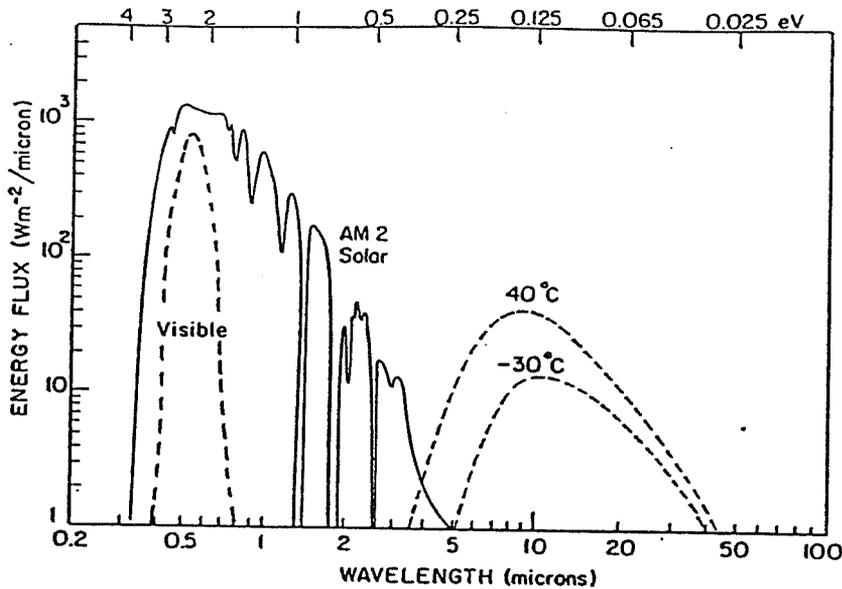
Optical switching devices known as "smart windows" and "chromogenic devices" can be used for the regulation of incident solar energy and glare in buildings, vehicles and aircraft. The world-wide production of flat glass is about 1 billion m<sup>2</sup> per year. In the U.S alone, glass production is about 470 million m<sup>2</sup> per year (1988), with about 25% for buildings and 11% for automobiles, so the potential for switching applications is very large. Just in a few years low-e coatings for windows have gained about 10% of the U.S. residential glazing market. Low-e or low emissivity coatings are used to reduce the radiative portion of heat transfer from glass surfaces. Emerging applications for chromogenic materials are automobile mirrors which can automatically regulate glare according to light levels. Prototypes are being tested for automobile sun roofs and visors. Future applications include automobile side and rear windows, architectural glazing and aircraft windows. Chromogenic devices can also be used for large-area information displays in applications where high switching speed is not required, such as for airport display boards. Photochromic glass for eyeglasses is one of the most mature chromogenic technologies. The function of a chromogenic device is to control the flow of light and solar energy through a window, according to an energy management scheme or the desire of the user. This technology could regulate lighting and heating levels for energy load reduction. Substantial savings in lighting and cooling energy consumption and equipment costs may be realized. From a privacy viewpoint, this technology may have a significant advantage over existing blinds and drapes. In the last few years there has been significant growing interest in this technology and it is expected to continue into the 21st century.

The basic property of a chromogenic material is that it exhibits a large change in optical properties upon a change in either electrical field, charge, light intensity, spectral composition, or temperature. This optical change results in a transformation from a highly transmitting state to a partly reflecting or absorbing state, either totally or partly over the visible and solar spectrum.

The physical phenomena of interest for optical switching processes can be classified in one of two categories, electrically activated or non-electrically activated. The electrically activated types include electrochromic, liquid crystals and dispersed particle devices (electrophoretic) and reversible electrodeposition. The non-electrically activated types include photochromic, and thermochromic materials. The former category has the advantage of user control and the latter category has the advantage of being self-regulating.

For chromogenic devices we are interested in the photopic (luminous), solar and thermal infrared spectra. These energy spectra are shown in Fig.1. A switching material-energy band matrix is shown in Table 1. Here all the possibilities for solar and thermal modulation are shown. However, it is not presently known if materials exist that have all the potential properties depicted. The next degree of complication would be to be able to vary all bands independent of each other.

Thin film fabrication is relevant to many of the chromogenic materials and devices. Several large-area technologies are useful, such as planar reactive d.c. magnetron sputtering, different varieties of chemical vapor deposition, and dip coating. High rate sputtering is advancing rapidly. The advent of rotating cathodes, with superior materials utilization, is likely to lead to a drop in manufacturing cost. Chemical vapor deposition (spray pyrolysis) is possible to coat directly on the float line of a glass manufacturing plant, which can give very inexpensive coatings of transparent conductors and other materials. This novel technique is now being extended to multilayer coating. Also, plasma enhanced chemical vapor deposition lends itself to very high deposition rates for certain compounds. Advances in fabrication technology will help reduce the cost of chromogenic windows. With these technologies there are still significant challenges for the process designer to adapt large-scale deposition technologies to the fabrication of square meter size multilayer electronic devices with high optical quality.



XBL 808-5758F

Fig. 1. Spectral distribution of the photopic or luminous, solar (air-mass 2), and blackbody thermal spectra.

Table 1. Chromogenic Materials Matrix

Visible	NIR	IR*	Description	Example	Usage
F	F	F	Fixed Passive Film	Glazing, Low-e Coating	Extensive
F	F	V	Changeable IR Emittance	Switch. Abs-Ref. Thermochromic/ Electrochromic	Research
F	V	F	Tunable Solar NIR	Electrochromic	Future glazings
V	F	F	Tunable Solar Visible	Photochromic/ Electrochromic/SPD.	Future glazings
F	V	V	Broadband IR	Thermochromic	Future glazings
V	F	V	Two-band ajd. (VIS & NIR)	None	None
V	V	F	Broadband Solar	Electrochromic/ Liquid crystals	Future glazings
V	V	V	All Band Variable	None	None

F: Fixed properties over the range specified.

V: Variable properties over the range specified.

VIS: Visible = 0.39 - 0.77 nm, NIR:Near-infrared = 0.77 - 2.5 nm and

IR: Infrared = 2.5-100 nm.

\*IR: Infrared properties are largely dependent upon the substrate, most substrates are opaque.

SPD: Suspended Particle Device

## ELECTRICALLY ACTIVATED DEVICES

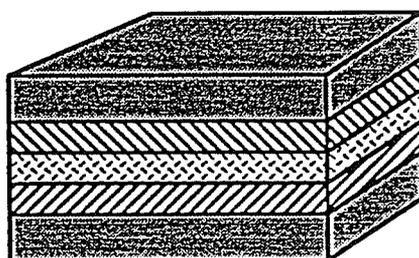
We begin our discussion with the electrically activated materials, since they are receiving so much attention for glazing applications. The electrically active materials consist of electrochromic, dispersed liquid crystals and suspended particle devices. The utilization of these materials for large-area switching creates a considerable challenge for the electrical engineer, materials scientist and optical designer.

Electrochromic Devices

Electrochromism is exhibited by several inorganic and organic compounds. Electrochromic materials change their optical properties due to the action of charge and ion movement induced by an applied field and can be changed back to the original state by field reversal. Color changes associated with ion insertion and extraction were reported for a sodium tungsten bronze as early as 1951. The potential usefulness of the phenomenon was not appreciated until the late 1960's. Typical materials used in today's devices are tungsten oxide ( $WO_3$ ) and nickel oxide or hydroxide ( $NiO$  or  $Ni(OH)_2$ ). Other inorganic materials that have gained research interest are  $MoO_3$ ,  $IrO_x$ ,  $Nb_2O_5$ ,  $MnO$ , and  $CoO_x$  films. The mechanism underlying the optical change, occurs in inorganic compounds by dual injection or ejection of ions ( $M$ ) and electrons ( $e^-$ ). A typical reaction for a cathodic coloring material is:  $WO_3$  (Transparent) +  $yM^+ + ye^- \leftrightarrow M_yWO_3$  (blue) where  $M = Li^+, H^+, Na^+$ , etc. A typical anodic reaction is:  $Ni(OH)_2$  (Transparent)  $\leftrightarrow NiOOH$  (bronze) +  $H^+ + e^-$ . It is evident that an electrochromic device must utilize an ion-containing material (electrolyte) in proximity with the electrochromic layer as well as transparent conductor layers for setting up a distributed electric field. Devices are designed in such a way that they shuttle ions and electrons back and forth into the electrochromic layer with applied potential. The major advantages of electrochromic materials are: they only require power during switching, have a long term memory (12-48 hr), require small voltage to switch (1-5 V), are specular in all conditions, have a large viewing angle and have the potential for large-area fabrication.

A window device can be fabricated from at least 3-5 layers consisting of two transparent conductors (TC), electrolyte (EL) or ion conductor (IC), ion storage layer (IS), and electrochromic layer (EC), as shown in Fig. 2. Research is needed to develop, better electrochromic materials with high cycle lifetimes, and short response times. New types of fast-ion conductors and solid electrolytes also require development for electrochromics to mature.

Transparent Conductor-TC  
Electrochromic-EC  
Ion Conductor-IC/Electrolyte-EL  
Ion Storage-IS  
Transparent Conductor-TC



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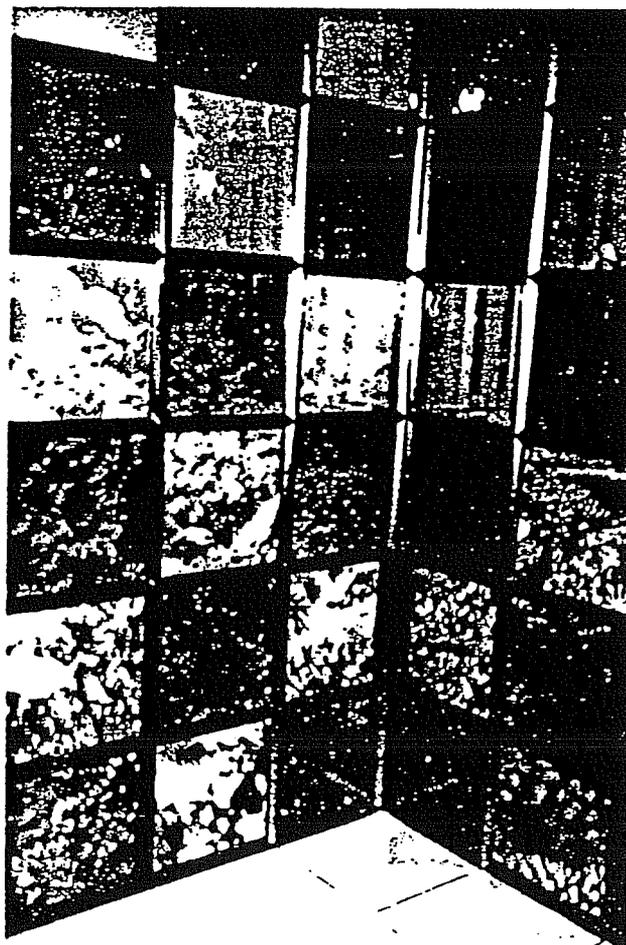
Liquid Device  
Electrolyte Device  
Ion Storage Layer Device  
Complimentary Electrochromic  
Combined Storage and Conductor

TC	EC-EL	TC		
TC	EC	EL	TC	
TC	EC	IC	IS-TC	
TC	EC	IC	EC	TC
TC	EC	IC	IS	TC

Fig. 2. Electrochromic device design schematic. Also, shown is a table of common device structures.

Organic electrochromics are based on the viologens, polyaniline, anthraquinones, diphthalocyanines, and tetrathiafulvalenes. With organics, coloration of a liquid is achieved by an oxidation-reduction reaction, which may be coupled with a chemical reaction. The organic electrochromics tend to suffer from problems with UV stability and secondary reactions during switching, these problems have slowed their development. The viologens are the most studied of the organic electrochromics. Related derivatives have been successfully used in switchable automobile mirrors and introduced as products by Gentex (Zeeland, MI) and Donnelly Corp. (Holland, MI). Another popular organic electrochromic is polyaniline (studied at the Univ. of Rhode Island, Providence, RI)

Several research groups are investigating electrochromic materials and devices. Asahi Glass (Yokohama, Japan) has introduced prototype windows that use  $\text{Li}^+$  ions for coloration of amorphous tungsten oxide ( $\alpha\text{-WO}_3$ ) using a polymer electrolyte. About two hundred 40x40 cm prototype electrochromic windows have been installed in the Seto Bridge Museum (Kojima, Okayama-Pref., Japan), shown in Fig. 3. Also, 50 windows have been installed in the Daiwa House (Mita-city, Hyogo-Pref., Japan). These prototype installations are the largest glazed areas of electrochromic glass seen to date in the world.



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Fig. 3. Photograph of the inside of the Seto Bridge Museum showing the Asahi Glass ECW electrochromic glass windows (underwater scene). Both the bleached and colored conditions are shown.

Nissan Motors (Yokosuka, Japan) with Central Glass (Tokyo, Japan) have developed an  $\alpha$ -LiWO<sub>3</sub>-Prussian Blue (Fe<sub>4</sub>(Fe(CN))<sub>6</sub>)<sub>3</sub> complementary electrochromic device. In this device two layers color together giving increased optical density. In 1987, at the Tokyo Auto Show Nissan displayed their electrochromic sunroof on the Cue-X concept car, shown in Fig. 4. An inorganic electrochromic mirrors based on  $\alpha$ -H<sub>x</sub>WO<sub>3</sub> are being developed for automotive use at Schott Glass (Weisbaden, FRG). It has the distinction of being the only true field-effect device using seven layers. Also, Nikon (Tokyo, Japan) and Ichikoh (Tokyo, Japan) have developed an inorganic electrochromic mirror for cars, based on tungsten oxide and iridium tin oxide. Nikon is also working on electrochromic eyeglasses. Also, devices based on  $\alpha$ -complementary WO<sub>3</sub> and  $\alpha$ -IrO<sub>2</sub> have been studied by EIC Labs (Norwood, MA) for NASA space applications. A truck mirror based on tungsten and nickel oxides is being developed by Donnelly and OCLI (Santa Rosa, CA). Another automotive mirror is being developed at Toyota Motors using tungsten oxide and a polyaniline laminated system. The Toyota technology may also be used for auto sunroof glazing.



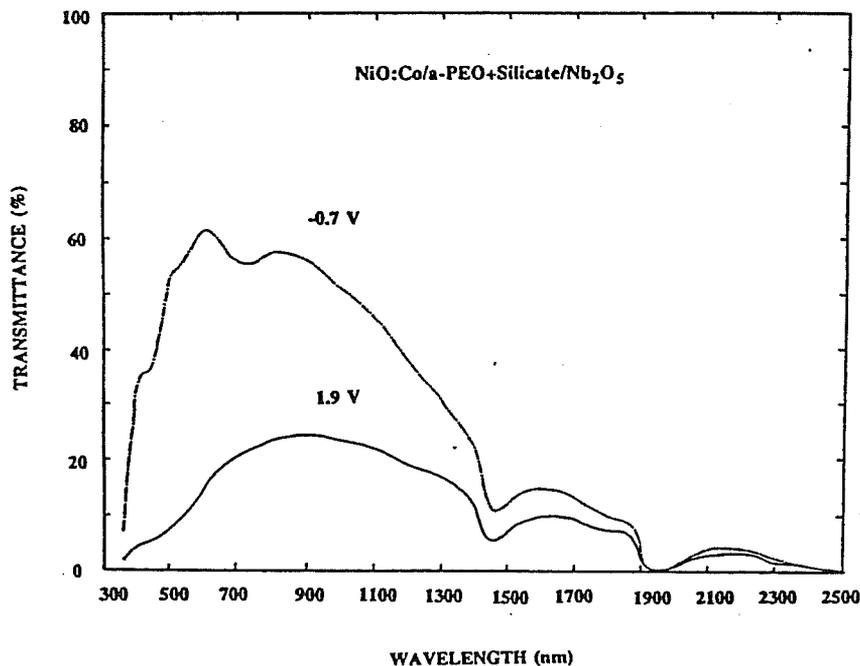
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Fig. 4. Prototype electrochromic electric sunroof made by Nissan Motors and Central Glass Co. It consists of four separate sunroof sections all colored to different degrees. The device consists of a complementary design using tungsten oxide and Prussian blue. (Photo provided by the Nissan Corp. Yokosuka, Japan)

Polycrystalline  $\text{WO}_3$  offers near-infrared modulation, which has the potential to control the infrared portion of the solar spectrum. Crystalline  $\text{WO}_3$  is being studied at Tufts University (Medford, MA) and EIC Labs (Norwood, MA). Near-infrared switching levels from 20% to greater than 75% have been achieved. Devices based on  $\text{c-WO}_3$  and  $\text{LiCoO}_x$  have been fabricated at Tufts.

Electrochromic  $\text{NiO}$ ,  $\text{WO}_3$ ,  $\text{NiO:Co}$ ,  $\text{MnO:Ni}$  and  $\text{Nb}_2\text{O}_5$  have been researched for devices at the Lawrence Berkeley Laboratory (Berkeley, CA). Also, a reversible ion storage polymer for these devices has been developed at Berkeley. The optical response for a device based on  $\text{NiO:Co/a-PEO}$  polymer/ $\text{Nb}_2\text{O}_5$  is shown in Fig.5. This device has photopic transmittance from 65% to 16% when fully switched.

From all these developments, it is evident that the smaller area switchable technology is moving to the marketplace. It will be followed by larger area devices for a wider range of applications in the years to come.



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Fig. 5. Solar optical response of a prototype nickel oxide/niobium oxide electrochromic device using a polymer ion conductor.

## Liquid Crystals

Liquid-crystal based systems offer another approach to electrically activated devices. The basic mechanism is to use an electric field, provided by two transparent electrodes, to change the orientation of liquid crystal molecules interspersed between the electrodes. The orientation of the liquid crystals changes the optical properties of the device. Open circuit memory is not possible. The most widely used type for electronic displays is the twisted nematic type. For windows, the twisted nematic type is not a good choice since it requires polarizers which reduce transmission and has fabrication size limitations, because of stringent gap spacing.

Two of the most important liquid crystal systems for large-areas are guest-host and polymer-dispersed or encapsulated devices. The guest-host type use dichroic dye molecules mixed with liquid crystals. The dye molecules can give modulated absorptance. The Asulab company in Switzerland is developing switchable goggles based on guest-host liquid crystals. The polymer dispersed type consists of nematic liquid crystals enclosed in micrometer-sized cavities. This cavity structure can give modulated light scattering using the Christiansen effect.

Dynamic scattering nematic liquid crystal glazings have been introduced by Taliq (Palo Alto, CA USA) as optical shutter materials. Significant research on this technology has been done at Kent State University (Kent, OH) and General Motors Research Labs. (Warren, MI). Commercial devices are based on NCAP (nematic curvilinear aligned phase) technology. With NCAP, the liquid crystals are encapsulated within an index matched polymer matrix. The composite polymer is fabricated between two sheets of  $\text{In}_2\text{O}_3:\text{Sn}$  coated polyester which serve as electrodes. The device can also be fabricated between two sheets of conductive glass. The switching effect of this device spans the entire solar spectrum, up to the absorption edge of glass or plastic. In the off-state, the device appears translucent white. When an electric field is applied, the liquid crystal droplets align with the field and the device becomes transparent, as shown in Figs 6 and 7 respectively. These devices operate at typically between 30-100V a.c., at less than  $20\text{W}/\text{m}^2$  but require continuous power to be clear. Examples of an application of a Taliq dispersed liquid crystal window is shown in Figs. 8 and 9. Dyes can be added to increase the range of switching in the visible region.

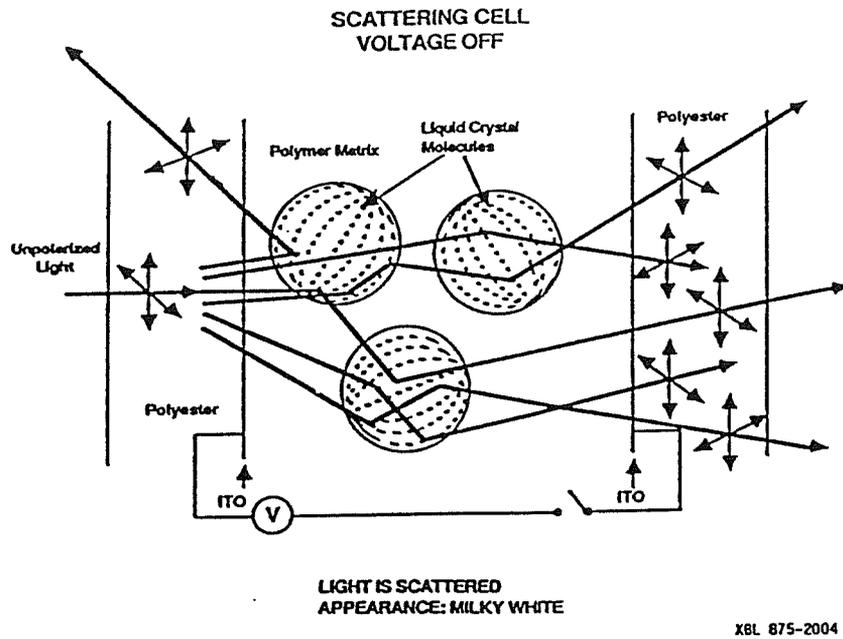


Fig. 6. Schematic of a dispersed liquid crystal device in the voltage-off state. (After van Konynenburg, Marsland and McCoy, 1987).

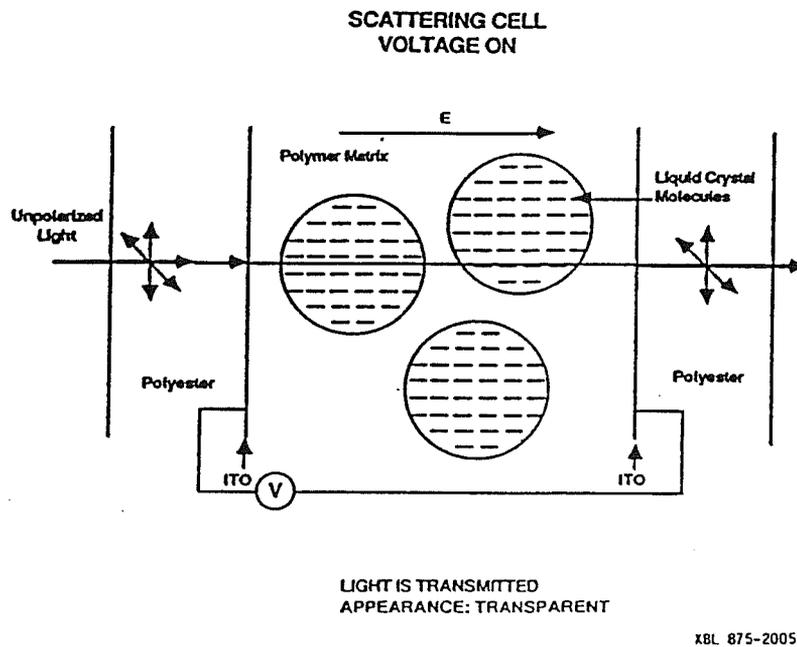
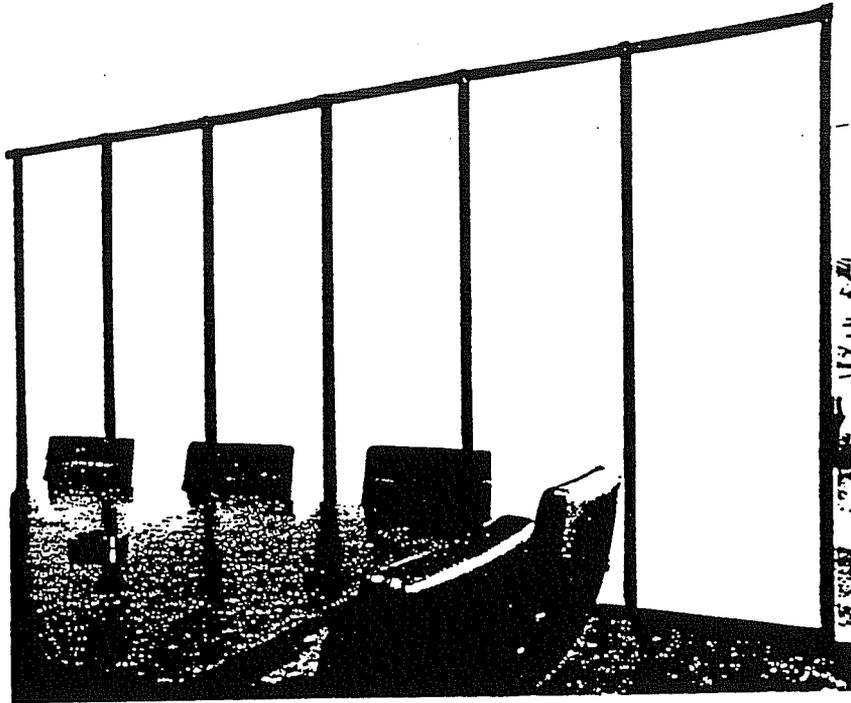
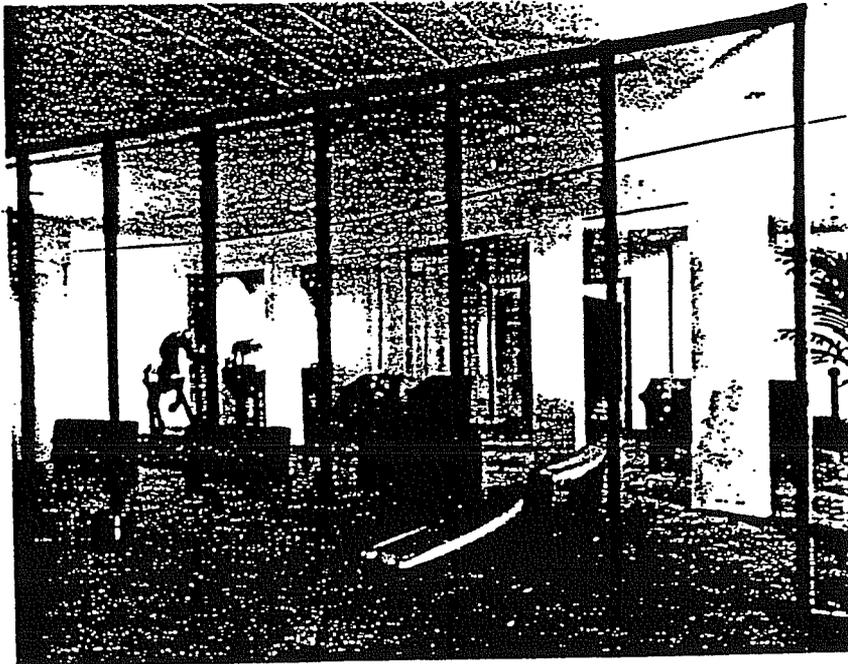


Fig. 7. Schematic of a dispersed liquid crystal device in the voltage on-state. (After van Konynenburg, Marsland and McCoy, 1987).



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Fig. 8. Photo of a Taliq dispersed liquid crystal device installed in an office building. Shown in the voltage-off condition. (Photo provided by the Taliq Corp, Palo Alto, CA.)



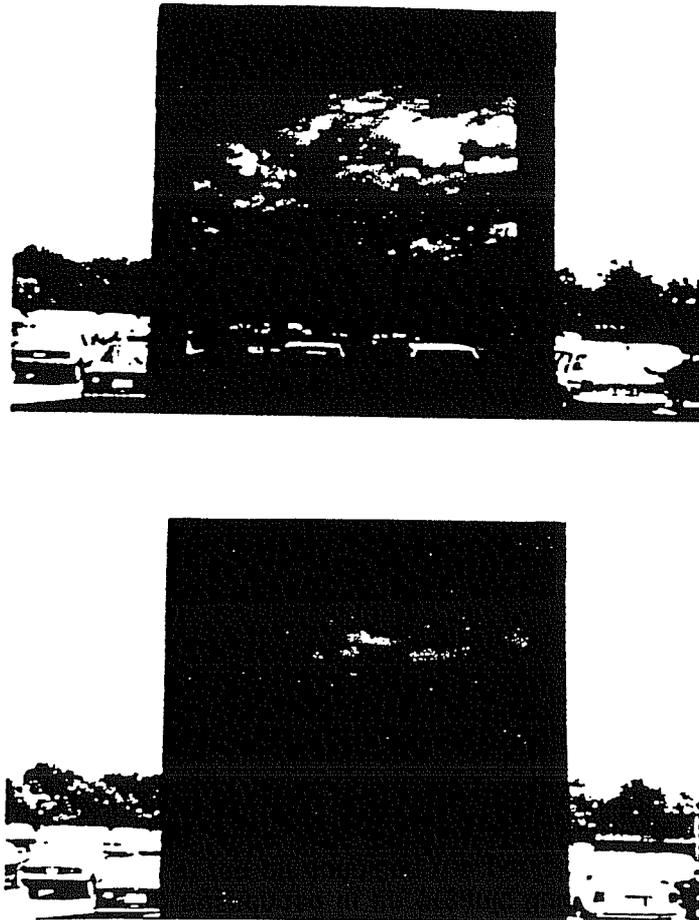
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Fig. 9. Photo of a Taliq dispersed liquid crystal device installed in an office building. Shown in the voltage-on condition. (Photo provided by the Taliq Corp, Palo Alto, CA.)

### Suspended Particle Devices

There has been work in suspended particle (electrophoretic) devices for many years. Its development has been slowed by a number of technological problems including long term stability, cyclic durability, particle settling and agglomeration and gap spacing control for large-areas. Recently many of these problems have been reduced or controlled. Commercial development of these devices for eyeglasses and windows is being done by Research Frontiers (Plainview, NY, USA) and Central Glass (Tokyo, Japan) and Nippon Sheet Glass (Itami City, Japan).

A suspended particle device consists of 3-5 layers. The active layer has needle shaped particles of polyimides or paraphathite (1 $\mu$ m long) suspended in an organic fluid or gel. This layer is laminated or filled between two parallel conductors. In the off condition the particles are random and light absorbing. When the field is applied the particles align with the field and transmission is increased. Typical transmission ranges are 20-60%, 10-50%, and 0.1-10%, with switching speeds of 100-200 ms. The voltage required for the device depends on thickness and ranges from 0-20 to above 150 VAC. An example of the switching effect seen in a suspended particle device is shown in Fig. 10.



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Fig. 10. Example of a suspended particle optical switching device shown in different conditions of coloration. (Photo provided by Research Frontiers, Plainview, NY, USA).

## NON-ELECTRICALLY ACTIVATED DEVICES

Photochromic Materials

Photochromic materials change their optical properties when exposed to light and revert to their original properties in the dark. Generally, photochromic materials are energy-absorptive. Basically, the phenomenon is the reversible change of a single chemical species between two energy states having different absorption spectra. Scientific discussions of photochromism date back to the 1880's. The phenomenon is widespread and occurs in many organic and inorganic materials. Photochromic organics include certain dyes, stereoisomers, and polynuclear aromatic hydrocarbons. Photochromism in organic materials is associated with heterolytic and homolytic cleavage, *cis-trans* isomerisation and tautomerism.

The inorganics include HgCNS, HgI<sub>2</sub>, Li<sub>3</sub>N, TiO<sub>2</sub>, ZnS, and alkaline earth sulfides and titanates. Many of these compounds are not pure phases as they require traces of a heavy metal or halogen to be photochromic. Glasses that exhibit photochromism are silver halide glasses, Ce, and Eu doped glasses and Hackmanite. Photochromic glasses developed by Corning Glass (Sullivan Park, NY, USA) are the most widely known of photochromic materials. They are used in ophthalmic glass. The glass shows good durability and fatigue-resistance during color/bleach cycling .

Photochromic metal-halide doped inorganic glasses absorb UV light, leading to disassociation reaction of metal-halide molecules, which in turn forms a color center in the visible region. The color centers are responsible for the coloration and absorption in the visible. When the UV light is removed the metal-halide molecule recombines by thermal processes. Probably the best known photochromic material is photochromic glass for ophthalmic glasses and goggles. Of all the photochromic materials much of the technical information is on metal-halide glasses. The typical optical response for a photochromic glass in the bleached and colored states is shown in Fig 11. A photochromic plastic has been developed by American Optical Corp. (Southbridge, MA, USA) and at PPG Industries (Monroeville, PA) using derivatives of spiroinodolinonaphthoxazine in a matrix of cellulose acetate butyrate and other plastics. Its spectral properties are shown in Fig.12. This material has been introduced in 1991 by PPG for ophthalmic use, but with future research may become useful for energy regulating glazings for solar energy control.

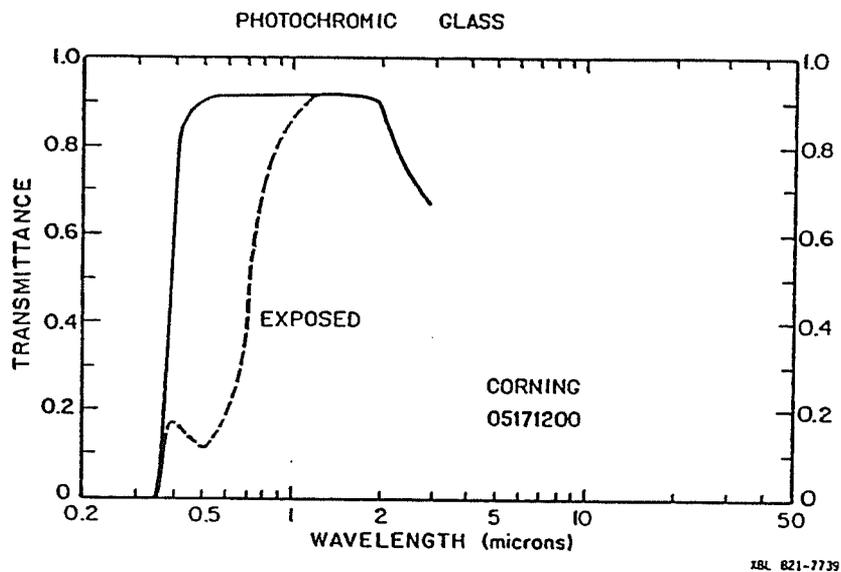


Fig. 11. Spectral response for a photogrey photochromic glass (Corning Glass, Corning, NY).

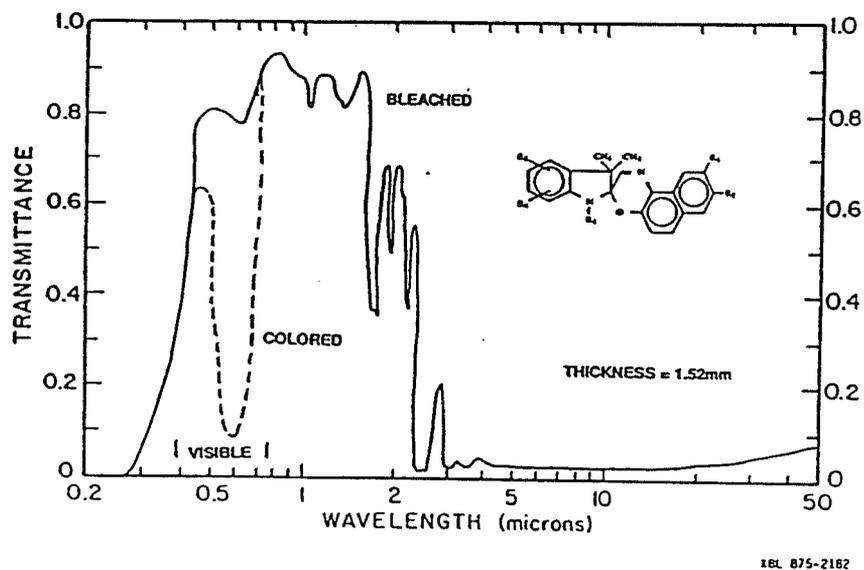


Fig. 12. Spectral response of an experimental photochromic plastic (American Optical Corp. Southbridge, MA). It is based on a spiroxazine derivative in cellulose acetate butarate.

## Thermochromic Materials

Thermochromic materials show a large change in optical properties with change in temperature. They return to their original properties when cooled to the starting temperature. Systematic studies of this phenomenon date back prior to the 1870's. Thermochromic materials change their properties by going through a thermally induced chemical reaction or by a phase transformation. Thermochromism can be due to equilibria between different molecular species, *cis-trans* isomerisation, crystal phase transitions, etc. Thermochromism is seen in a large number of organic compounds (Day, 1963). Organic compounds in the anil, spiropyrans, polyvinyl acetal resins, and hydroxide groups exhibit thermochromism. Also, polymer-based thermochromic "cloud gels" are being developed for window applications by the Fraunhofer Institute for Building Physics (Stuttgart, Germany, shown in Fig. 13).

Inorganic thermochromic compounds include AgI, Ag<sub>2</sub>HgI<sub>4</sub>, Cd<sub>3</sub>P<sub>3</sub>Cl, HgI, HgI<sub>2</sub>, SrTiO<sub>3</sub>, along with various cobalt, copper and tin complexes. Inorganic fibre/liquid composites can show thermochromism via the Christiansen effect. Of considerable interest are thin films of certain transition metal oxides and related compounds, which transform from semiconducting to metallic state when a certain "critical" temperature is exceeded (known as the Mott transition compounds). Such materials, when perfected, can be used to control both the solar transmittance and infrared emittance of a glazing or surface. Some of these compounds are Fe<sub>3</sub>O<sub>4</sub>, FeSi<sub>2</sub>, NbO<sub>2</sub>, NiS, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>5</sub>O<sub>9</sub>, VO<sub>2</sub>, and V<sub>2</sub>O<sub>3</sub>. A thermal conductivity plot for some compounds is shown in Fig. 14. The key issues concerning these compounds are control or modification of the transformation temperature, transmission in the bleached state and magnitude of the optical density change and electron concentration change after switching. For window applications some research has been done on VO<sub>2</sub> at the Honeywell Corp. (Minneapolis, MN). By substitutional doping of vanadium in VO<sub>2</sub>, alteration of the transformation temperature can be achieved. Compounds of V<sub>1-x</sub>W<sub>x</sub>O<sub>2</sub> have shown large changes in transition temperature but unfortunately smaller changes in conductivity during switching compared to VO<sub>2</sub>.

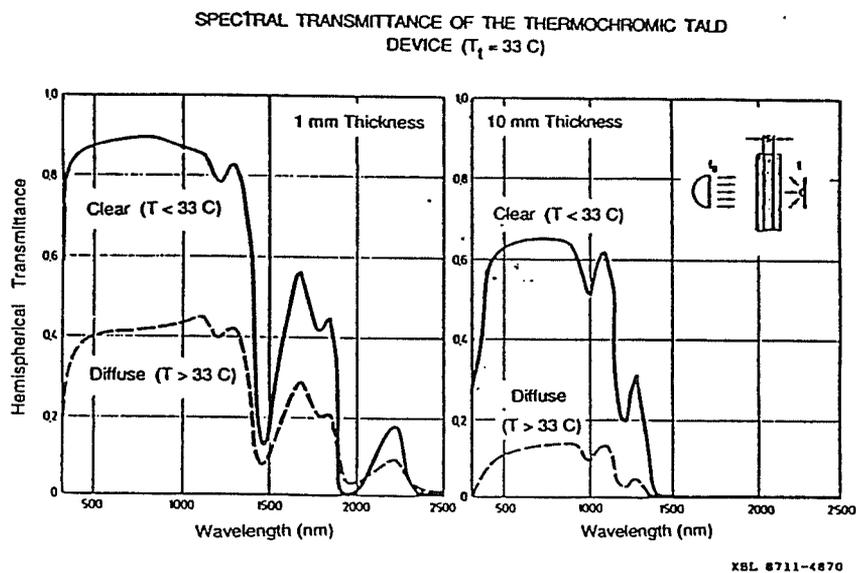


Fig. 13. Spectral response of the TALD thermochromic polymer window. (after data supplied by the, Fraunhofer Institute for Building Physics, Stuttgart, Germany )

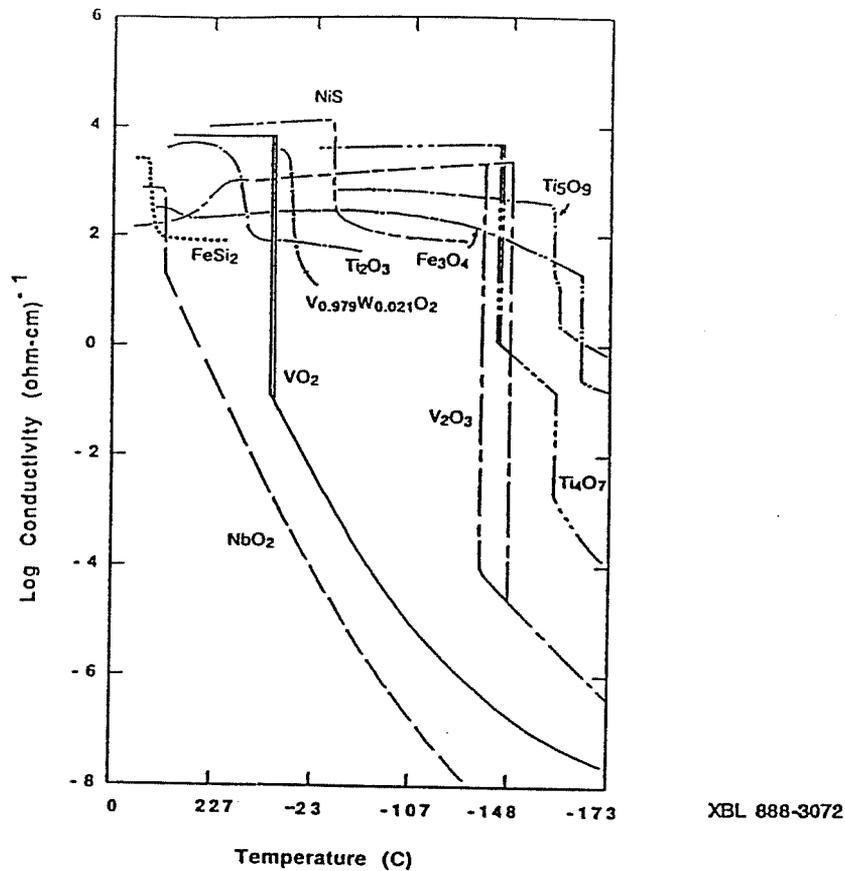


Fig. 14. Conductivity-temperature plot for several thermochromic compounds showing the Mott-transition effect.(after data from Honeywell Corp, Minneapolis, MN ).

## CONCLUSIONS

The concept of the chromogenic device has been discussed for large-area applications. The technologies covered were electrochromism, dispersed liquid crystals, suspended particle devices, photochromism and thermochromism. This technology embraces a fascinating mix of basic work and applications which ultimately may lead to better buildings and vehicle glazing, and display technology. In a number of applications, it will help lower of the demands on precious non-renewable fuels for lighting and cooling. The prospects are great, and so are the scientific and technological challenges of large-area chromogenics.

Electrochromism has great potential for large-area applications. There are several promising devices for window glazings. For the electrochromic layer, tungsten trioxide is the most research material. However, there are many other candidate materials, primarily among the transition metal oxides and among several classes of organics. In fact, the study of "unconventional" inorganic or organic electrochromic materials will be a fertile area for research and development for years to come. In the future, the developments will lie in the designing of the appropriate ionic and electronic materials to make devices durable over the long term.

Liquid-crystal-based materials and devices have a very good future but are restricted by three characteristics: the unpowered state is diffuse, haze remains in the activated (transparent) state and UV stability is poor. The residual haze problem can probably be alleviated by better control over the formation and processing of the liquid crystal emulsion. The UV stability will have to be improved, but this possible too. The cost of devices will have to decline for widespread use. One of the significant costs is in the transparent conductors. It is expected that with further research and new materials, such as doped ZnO and polymer conductors, this cost will decrease.